

NOVEL HIGH MOLECULAR WEIGHT ASSOCIATIVE AMPHOTERIC POLYMERS AND USES THEREOF

The invention concerns novel associative amphoteric polymers for increasing the
5 viscosity of aqueous solutions, as well as aqueous compositions containing said polymers.

By definition, we say that a polymer is polymer viscosifying when it increases the
viscosity of the solutions in which it is dissolved.

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Among the viscosifying polymers for aqueous solutions included in the state of
the art, synthetic polymers such as poly(meth)acrylamides, which may be partially
hydrolysed, and poly(meth)acrylates and their copolymers are particularly well
known. These polymers develop viscosity due to their molar mass and to
15 interchain ionic repulsions. The mechanism causing viscosity is related to an
increase in hydrodynamic volume and interchain repulsions.

However, in the presence of electrolytes, surfactants or a high temperature of use,
these polymers do not develop good thickening properties, leading to a sharp
20 decrease in their viscosifying power.

To improve the performances of the aforementioned synthetic polymers, they
have been modified by adding hydrophobic groups. The polymers thus obtained
(the minority of which have apolar unit cells and the majority of which have
25 hydrophilic unit cells) are called "associative". They require high molecular mass
and are characterised in that, when they are placed in solutions, their hydrophobic
groups join together to limit interactions with water. The drop in viscosity related
to the presence of electrolytes, surfactants or high temperatures, source of a drop
in hydrodynamic volume, is compensated for by interchain attractive interactions.

The vast majority of the most common acrylic associative polymers come in the form of an emulsion (in water or reverse or aqueous dispersion). It should be pointed out that reverse emulsion polymerisation is a preferred method well
5 known to those skilled in the art. It notably provides acrylic polymers with high molecular weight and may contain a reasonably high concentration of polymers while remaining fluid. Moreover, the large specific surface of the dispersed phase of the polymer makes solubilisation or swelling of the polymer very rapid.

10 The hydrophobic monomers used in preparing these polymers may be of 2 types: non-ionic and/or ionic.

Among the non-ionic hydrophobic monomers, we can mention:

- industrially available (meth)acrylic acid esters with an alkyl chain or
15 ethoxylated,
- and acrylamide derivatives with an alkyl or dialkyl chain requiring, for copolymerisation, difficult implementation not yet having undergone any industrial development.

20 At the same time, the use of hydrophobic ionic monomers has also been described. This mainly concerns:

- cationic allyl derivatives, which have very poor reactivity leading to derivative compounds which are harmful to the desired applications as they form insoluble chains.
- 25 - or hydrophobic ionic acryloyl derivatives (anionic or cationic), these being mentioned as potential monomers but very rarely exemplified and never described in powder form.

During research on the preparation of new amphoteric polymers used to increase the viscosity of aqueous compositions, whatever their salinity, their surfactant composition or their temperature, the applicant took a closer look at associative amphoteric polymers.

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The previous state of the art shows:

- 10 - Patent US 5071934 concerning the preparation of associative cationic polymers which can be interpreted as amphoteric in extreme cases, obtained in an emulsion. No examples are given concerning polymerisation for obtaining amphoteric polymers: the examples deal with copolymerisation in emulsions of acrylamide, methacrylamido-propyl trimethyl-ammonium chloride (MAPTAC) and dimethyl aminopropylamine (DMAPA) quaternised with an alkyl chain with 8 to 14 carbons.
- 15 - Patent WO 01/40318 which protects a new method of synthesis in a liquid solution of hydrophobic polymers which may be amphoteric but is not exemplified.
- 20 - Exxon patent US 4650848 which describes non-charged associative hydrophobic AMD/AMD terpolymers / betaine: the amphoteric aspect of these polymers is introduced by a zwitterionic monomer which alone carries both charges in exactly equal quantities.
- 25 - Calgon patent WO 01/06999 concerning low molecular weight (less than $10,000 \text{ g.mol}^{-1}$) hydrophobic amphoteric polymers, whose apolar groups are carried by an anionic and/or non-ionic monomer. Given their low molecular weight, these polymers have no viscosifying effect.

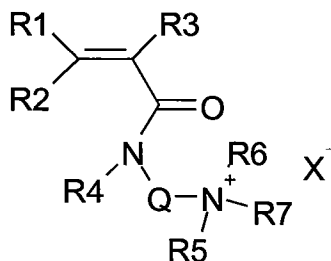
None of aforementioned products, however, has to date undergone industrial development due to their inherent inconveniences: lack of viscosity, stability over time, temperature stability, and/or problems related to their preparation or implementation.

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Description of the invention

The applicant has discovered and developed novel associative acrylic amphoteric polymers, characterised in that they have a molecular weight of at least
10 50,000 g/mol, in practice between 50,000 g/mol and $30 \cdot 10^6$ g/mol, and in that they include:

- at least one acrylamide-derived cationic monomer containing a hydrophobic chain and with the general formula:



15 where:

R1,R2,R3,R4,R5,R6, independently, a hydrogen or an alkyl chain containing 1 to 4 carbons

Q: an alkyl chain containing 1 to 8 carbons

R7: an alkyl or arylalkyl chain containing 8 to 30 carbons

20 X: a halide selected from the group including bromide, chloride, iodide, fluoride or a counterion with a negative charge.

- between 1 and 99.9 mole % of at least one anionic monomer. The useful anionic monomers in this invention can be selected from a wide group. These
25 monomers may present acrylic, vinyl, maleic, fumaric or allyl functionalities and may contain a carboxy, phosphonate, sulfonate or other group with an

anionic charge, or the ammonium salt or alkaline-earth metal salt or alkaline metal salt corresponding to such a monomer. Examples of suitable monomers include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid and strong-acid monomers, for example with a sulfonic or
5 phosphonic acid-type function such as 2-acrylamido-2-methylpropane sulfonic acid, vinylsulfonic acid, vinylphosphonic acid, allylsulfonic acid, allylphosphonic acid, styrene sulfonic acid and their water-soluble salts of an alkali metal, alkaline-earth metal and ammonium.

- and between 1 and 99 mole % of at least one non-ionic hydrosoluble monomer.
- 10 The useful non-ionic monomers in this invention can be selected from the group including water-soluble vinyl monomers. The preferred monomers belonging to this category are advantageously selected from the group including acrylamide and methacrylamide, N-isopropylacrylamide, N-N-dimethylacrylamide and N-methylolacrylamide. N-vinylformamide, N-vinyl
15 acetamide, N-vinylpyridine and/or N-vinylpyrrolidone can also be used. Acrylamide will be the preferred non-ionic monomer.

Surprisingly, it was discovered that it is possible to obtain associative polymers which, with an equal molecular weight and whatever the conditions of use,
20 develop a viscosifying effect in the aqueous composition greater than that of the former state of the art, using an amphoteric polymer according to the invention, based on one or a mixture of acrylamide-derived hydrophobic cationic monomers, based on one or a mixture of anionic monomers and based on one or a mixture of non-ionic hydrosoluble monomers.

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Along with the improved viscosifying effect, the selection of this type of polymer also provides shorter solution times.

The polymers in the invention do not require developing a particular polymerisation process. They can be obtained by all the polymerisation techniques well known to those skilled in the art (solution polymerisation, gel
 5 polymerisation, precipitation polymerisation, emulsion polymerisation [aqueous or reverse], whether followed or not by spray drying, suspension polymerisation, micellar polymerisation, whether followed or not by a precipitation step).

The invention also concerns the previously described branched and/or cross-
 10 linked associative amphoteric polymers. The usable branching agents (cross-linking agents) are N-methylol acrylamide, methylene bis acrylamide, allyl ethers of sucrose, diacrylates, divinyls and all other multifunction compounds which can cause branching. One could also use one of the known branching agents for diallylated compounds such as methyl triallyl ammonium chloride, triallylamine,
 15 tetraallyl ammonium chloride, tetra allyl oxyethane, tetra allyl ethylene diamine and, more generally, all polyallylated compounds. It is also possible to make post-cross-linked polymers, for example by amidation reaction, esterification reaction, gamma ray treatment, etc.

20 The invention also concerns the use of the aforementioned associative polymers, whether branched and/or cross-linked or not, as well as the gels containing them in the oil, paper, water treatment, mining, cosmetics, textile and detergent industries.

25 The associative amphoteric polymers in the invention are preferably polymers with:

- between 0.005 and 10 mole % hydrophobic cationic monomer
- between 5 and 90 mole % of at least one anionic monomer, advantageously acrylic acid and/or methacrylic acid and/or 2-acrylamido-2-methylpropane
 30 sulfonic acid and their salts;

- and between 5 and 90 mole % of at least one hydrosoluble non-ionic monomer, advantageously acrylamide and/or methacrylamide and/or N-isopropylacrylamide and/or N-N-dimethylacrylamide and/or N-vinylformamide and/or N-vinyl acetamide and/or N-vinylpyrrolidone.

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According to an advantageous embodiment, the associative polymers contain between 0.01 and 5 mole % of hydrophobic monomers and between 10 and 60 mole % of an anionic monomer and between 35 and 90 mole % of a non-ionic monomer.

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Preferably, the associative polymers contain between 0.02 and 2 mole % of hydrophobic monomers and between 10 and 50 mole % of an anionic monomer: acrylic acid, methacrylic acid and/or 2-acrylamido-2-methylpropane sulfonic acid and their salts, and between 48 and 90 mole % of a non-ionic monomer: acrylamide and/or methacrylamide and/or N-isopropylacrylamide and/or N-N-dimethylacrylamide and/or N-vinylformamide and/or N-vinyl acetamide and/or N-vinylpyrrolidone.

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The acrylamide-derived hydrophobic cationic monomers preferred for the invention are N-acrylamidopropyl-N,N-dimethyl-N-dodecyl ammonium chloride (DMPA Cl(C12)), N-methacrylamidopropyl-N,N-dimethyl-N-dodecyl ammonium chloride (DMPMA Cl(C12)), N-acrylamidopropyl-N,N-dimethyl-N-dodecyl ammonium bromide (DMPA Br(C12)), N-methacrylamidopropyl-N,N-dimethyl-N-dodecyl ammonium bromide (DMPMA Br(C12)), N-acrylamidopropyl-N,N-dimethyl-N-octadecyl ammonium chloride (DMPA Cl(C18)), N-methacrylamidopropyl-N,N-dimethyl-N-octadecyl ammonium chloride (DMPMA Cl(C18)), N-acrylamidopropyl-N,N-dimethyl-N-octadecyl ammonium bromide (DMPA Br(C18)), N-methacrylamidopropyl-N,N-dimethyl-N-octadecyl ammonium bromide (DMPMA Br(C18)).

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We should point out that, to facilitate the addition of hydrophobic cationic monomers during polymerisation, those skilled in the art are aware that surfactants, whether ionic or not, can be used. In the context of this invention, the quantity of surfactant added is, however, much lower than the quantities used in micellar polymerisation (which are approximately 20 moles and more of surfactant per mole of hydrophobic monomer).

Likewise, the use of cosolvents such as tert-butanol, isopropanol, butanol, hexanol, pentanol, glycerol, etc. may be envisaged to help solubilise these monomers.

Moreover, optionally and in combination with the aforementioned monomers in the invention (acrylamide-derived hydrophobic cationic + anionic + non-ionic), one or more other monomers, whether ionic or not, hydrosoluble or not, may also be used in proportions preferably less than 20 mole %. For example, one may use monomers such as dialkylaminoalkyl (meth)acrylate, dialkylaminoalkyl (meth)acrylamide, diallylamine, methyldiallylamine and their quaternary ammonium salts or acid salts, etc., acrylamide derivatives such as N-alkylacrylamides, for example N-tert-butylacrylamide, octylacrylamide as well as N,N-dialkylacrylamides such as N,N-dihexylacrylamide, etc., derivatives of acrylic acid such as hydroxyalkyl acrylates and methacrylates or other monomers, whether ionic or not, hydrosoluble or not, such as allyl derivatives, styrene, acrylate esters which may contain ethoxylated chains or not terminating with an alkyl or arylalkyl chain...

Preferably, the associative polymers in the invention come in a dry, powder or granular form and are obtained directly by gel polymerisation, precipitation polymerisation or suspension polymerisation.

According to another characteristic, the molecular weight of the associative amphoteric polymer is greater than 50,000, advantageously greater than 100,000

and preferably greater than 200,000 g/mol. In practice, the polymers are used at a concentration greater than 500 ppm, preferably greater than 800 ppm and preferably greater than 1,000 ppm.

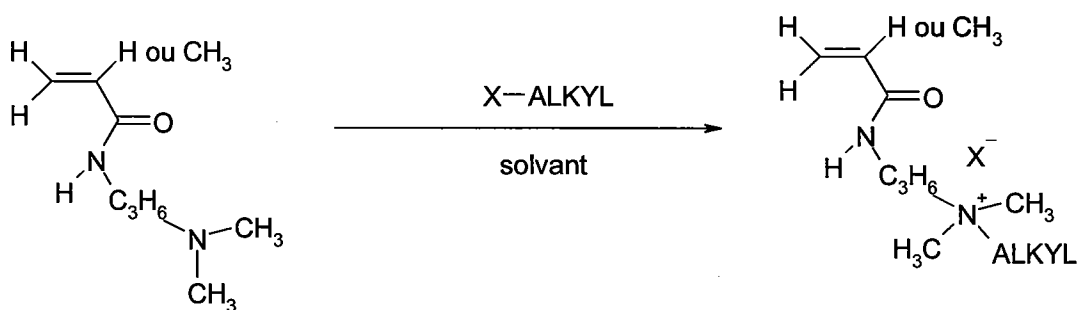
- 5 The invention also concerns an aqueous composition containing the aforementioned associative polymers used as viscosifying agents.

The invention will now be fully illustrated using the following non-limiting examples, and notably which will not be considered as being limited to the
10 compositions and forms of the polymers.

EXAMPLES

Cationic monomer synthesis

- 15 The hydrophobic cationic monomers derived from acrylamide or methacrylamide used in the examples were obtained using the general preparation scheme well known to those skilled in the art and as described below. This entails a quaternisation reaction of an N,N-dimethylaminopropyl(meth)acrylamide (DMAP(M)A) molecule by an alkyl or arylalkyl halide, obtained in a solvent
20 medium at 50°C. The general process of synthesis is notably described in example 1 of patent US 3948979, where N,N-dimethylaminoethyl acrylate has been replaced by N,N-dimethylaminopropylacrylamide (examples A) or by N,N-dimethylaminopropylmethacrylamide (examples M).



- 5 ALKYL: corresponding to an alkyl or arylalkyl chain with 8 to 30 carbons
 X: a halide which may be bromide, chloride, iodide, fluoride, or any counterion with a negative charge.

Preparation of the polymer by gel polymerisation (examples g: Ag or Mg):

- 10 In a beaker, dissolve x mole % of an acrylamide-derived hydrophobic cationic monomer, y mole % of acrylic acid, z mole % of acrylamide in water to obtain a 30% active ingredient content. The aforementioned additives may advantageously be added at this point to improve the solubilisation of the monomers. The sum of x+y+z is equal to 100. The solution is then stirred, cooled and neutralised by
- 15 adding soda. The solution is then placed in a Dewar vessel and degassed with a nitrogen flow to remove the oxygen.

Polymerisation is initiated using a red/ox pair. The temperature rises adiabatically.

- 20 The gel obtained is left in the Dewar vessel for 3 hours. It is then ground and dried overnight in an oven. A white powder is obtained and is ground once again.

Preparation of the polymer by precipitation polymerisation (examples p: Ap or Mp):

The process used is described in example 3 of Rohm & Haas patent EP 63018, adapted to our monomers.

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For each polymer obtained, the molar masses were determined by static light scattering.

EXAMPLE 1: viscosifying effect of the polymers in the invention in relation to their conditions of use

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The powders obtained were solubilised in various brines and the viscosity of the solutions was measured under different conditions of shearing and temperature. The results are given in tables 1, 2 and 3.

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Unless indicated, the counterion of the cationic monomer is a chloride, x corresponds to the mole percentage of the hydrophobic cationic monomer(s) and y corresponds to the mole percentage of the anionic monomer.

20 **Table 1:** measurement of the viscosity of the associative amphoteric products in deionised water at 20°C.

	R7	x/y mole %	M _w (10 ⁶ g.mol ⁻¹)	C (ppm)	Viscosity (cps) at 7 s ⁻¹	Viscosity (cps) at 100 s ⁻¹
Ag1	C ₁₂ H ₂₅	0.7 / 27	6.4	10,000	9,780	685 ^a
Ap2	C ₁₈ H ₃₇	5 / 20	0.2	40,000	2,350	660 ^a
Ag3	C ₁₂ H ₂₅	1 / 27	2.5	5,000	1,040	205 ^a

Table 2: measurement of the viscosity of the associative amphoteric products in brines at 24°C.

	R7	x / y mole %	M _w (10 ⁶ g.mol ⁻¹)	C (ppm)	Salt concentration in the brine (ppm)	Viscosity (cps)
Ag4	C ₁₈ H ₃₇	0.035 / 30	16.8	1,000	58,500	9.8 ^b
Mg4	C ₁₈ H ₃₇	0.035 / 30	16.8	5,000	5,700	1,350 ^c
Ag5	C ₁₂ H ₂₅	0.4 / 25	6.4	1,000	58,500	5.6 ^b
Ag6 ^m ,r	C ₁₂ H ₂₅	0.4 / 25	6.4	5,000	5,700	3,100 ^c
Ag7	C ₁₂ H ₂₅ /C ₁₈ H ₃₇	(0.5 / 0.05) / 30	6.4	5,000	5,700	10,000 ^c
Ap8	C ₁₂ H ₂₅	5 / 20	0.2	40,000 0	5,700	165 ^a
Ag9 ⁿ	C ₁₂ H ₂₅	0.4 / 27	2.5	5,000	0	3,000 ^c

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Table 3: measurement of the viscosity of the associative amphoteric products at different temperatures

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					Salt		
	R7	x / y mole %	M _w (10 ⁶ g.mol ⁻¹)	C (ppm)	concentration in the brine (ppm)	T (°C)	Viscosit y (cps)
Mg4	C ₁₈ H ₃ 7	0.035 / 30	16.8	1,500	5,700	70	70 ^d
Ag10 ^{o,r}	C ₁₂ H ₂ 5	0.6 / 25	6.4	2,000	10,800	65	300 ^a
Ag11 ^{p,r}	C ₁₂ H ₂ 5	0.6 / 27	6.4	1,500	32,800	70	80 ^d
Ag12 ^q	C ₁₂ H ₂ 5	0.4 / 20	6.4	5,000	10,800	50	3,600 ^a
Ag13 ^r	C ₁₂ H ₂ 5	0.7 / 27	6.4	2,000	10,800	65	380 ^a

C: concentration of the polymer in the brine, in ppm.

- a: viscosity was measured with a Carri-Med (model CSL 100) with cone-plate geometry (diameter = 6 cm, angle = 2°) at 7 s⁻¹ and 100 s⁻¹.
- b: measurement performed with a Brookfield viscometer, model LVT, at 60 rpm.
- c: measurement performed with a Brookfield viscometer, model DV-II+, at 30 rpm.
- d: viscosity was measured with a Brookfield viscometer, model LVT, at 6 rpm.
- m: polymer obtained in the presence of a cross-linking agent: 3 ppm of methylene bis acrylamide (MBA).
- n: polymer containing 1 mole % of tert-octylacrylamide.
- o: polymer containing 2 mole % of N-isopropylacrylamide.
- p: polymer containing 2 mole % of 2-acrylamido-2-methylpropane sulfonic acid.
- q: polymer containing 2 mole % de N-vinylpyrrolidone.

r: the counterion of the hydrophobic monomer is not a chloride but rather a bromide.

EXAMPLE 2: relative viscosity test

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To precisely compare the efficacy (viscosifying power) of the products in the invention, various polymers were prepared under strictly identical conditions: same procedure (cf. preparation of the polymer) and same molar compositions, according to the following table.

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	Cationic monomer			Non-ionic monomer	Anionic monomer
	Hydrophobic		Non hydrophobic	Hydrophobic	Non-hydrophobic
	Acrylamido-type	Allyl-type		Acrylate-type	
Inv.	YES				YES
xanio	NO	NO	NO	NO	YES
xampho	NO	NO	YES	NO	YES
xHampho	NO	NO	YES	YES	YES
xHLampho	NO	YES	NO	NO	YES
xHcatio	YES	NO	NO	NO	NO

The viscosity of the products noted x (V_x) was compared with that of the polymers in the invention (V_{inv}) under various conditions (deionised water, brine, at different concentrations and at different temperatures).

15

Coefficient R, which is expressed in a percentage, is defined by the following relation:

$$R = ((V_{inv} - V_x) / V_x) \times 100$$

The higher R is, the more the viscosifying power of the polymers in the invention differs from that of the “standard” polymers in the industry.

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Table 4: measurement of coefficient R in relation to a polymer obtained by gel polymerisation and containing 0.035 mole % of a cationic monomer and 30 mole % of an anionic monomer (the polymer used as the reference is **Ag4**).

- 10 Viscosity measurements performed at 5,000 ppm of polymer with Carri-Med at $7s^{-1}$ at 20°C. The brine at 5,700 ppm of salts contains 108 ppm of divalent ions (calcium chloride and magnesium chloride).

Products	Deionised water	Brine at 5,700 ppm	Deionised water
	20°C	20°C	70°C
xanio	+ 64%	+ 249%	+ 22%
xampho	+ 61%	+ 254%	+ 25%
xHampho	+ 8%	+ 7%	+ 130%
xHLampho	+ 21%	+ 132%	+ 19%
xHcatio	+ 2,000%	insoluble	+ 3,800%

- 15 **Table 5:** measurement of coefficient R in relation to a polymer obtained by gel polymerisation and containing 0.6 mole % of a cationic monomer and 27 mole % of an anionic monomer (the polymer in the invention used as the reference is **Ag11**).

- 20 Viscosity measurements performed at 1,500 ppm of polymer with Carri-Med at $7s^{-1}$. The brine at 32,800 ppm of salts contains 1,040 ppm of divalent ions (calcium chloride and magnesium chloride).

Products	Deionised water	Brine at 32,800 ppm	Deionised water
	20°C	20°C	70°C
xanio	+ 41%	+ 135%	+ 800%
xampho	+ 38%	+ 130%	+ 750%
xHampho	+ 11%	+ 31%	+ 208%
xHLampho	+ 100%	insoluble	+ 140%
xHcatio	+ 400%	+ 82%	+ 230%

Table 6: measurement of coefficient R in relation to a polymer obtained by precipitation polymerisation and containing 5 mole % of a cationic monomer and 20 mole % of an anionic monomer (the polymer in the invention used as the reference is **Ap8**).

Viscosity measurements performed at 40,000 ppm of polymer with Carri-Med at $7s^{-1}$. The brine at 5,700 ppm of salts contains 108 ppm of divalent ions (calcium chloride and magnesium chloride).

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Products	Deionised water	Brine at 5,700 ppm	Deionised water
	20°C	20°C	70°C
xanio	+ 1,100%	+ 1,150%	+ 1,570%
xampho	+ 1,000%	+ 1,130%	+ 1,500%
xHampho	+ 163%	+ 790%	+ 4,400%
xHLampho	+ 28%	+ 30%	+ 20%
xHcatio	+ 20%	+ 50%	+ 40%

CONCLUSION (tables 1 to 6)

It has been observed that, according to the invention, the use of an amphoteric polymer based on a hydrophobic cationic monomer derived from acrylamide or methacrylamide increases the viscosity of deionised water solutions, but also of saline solutions.

This effect of increasing viscosity may even be obtained with polymers containing very little hydrophobic cationic monomer and even at low polymer concentrations (<1,000 ppm).

The gain in viscosity can also be observed at different temperatures, at different shear rates and with different measurement methods.

Moreover, the novel associative amphoteric polymers in the invention, under identical conditions of molecular weight and molar composition (anionicity and/or cationicity), demonstrated a level of performance (gain in viscosity) significantly much higher than that obtained with the “standard” polymers (tables 4 to 6).

Given their physical properties, the polymers in the invention are useful ingredients for increasing the viscosity of all water-based compositions.

The invention also covers all forms of embodiment and all applications which will be directly accessible to those skilled in the art upon reading this application, through his/her own knowledge and possibly through simple routine tests.